Identification and Comparison of Solvents and Paint Removers as Alternatives to Methylene Chloride in Paint Removal Applications

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Abstract

California's Safer Consumer Products program has selected methylene chloride paint remover as a "Priority Product". As a manufacturer of methylene chloride paint removers, WM Barr will be required to evaluate alternative products that could be used in place of methylene chloride. This study compares the performance of methylene chloride paint removers to 22 alternative solvents currently used in non-methylene chloride paint removers or solvents proposed as a replacement by chemical manufacturers. The performance of 26 non-methylene chloride paint remover formulations currently available was compared to three methylene chloride based paint removers as well as 5 formulations using solvents with removal potential found in the neat solvent study. The solvents and paint removers were tested on wood panels treated with multiple layers of an oil-based alkyd paint, a solvent-borne epoxy paint and an OEM automotive finish. For chemically resistant oil-based alkyd, solvent--borne epoxy paints and OEM Automotive Coatings, only methylene chloride based paint removers were determined to be effective.

1. Background

Methylene chloride has been the preferred solvent for use in paint removers for seventy years. Before methylene chloride was introduced most paint removers were benzene based and thus were extremely flammable. The flammability resulted in many fires causing injury and death. Methylene chloride paint removers rapidly replaced benzene removers because they were non-flammable and very effective in removing coatings quickly. Physical characteristics give the methylene chloride molecule the ability to soften or dissolve chemically resistant coatings and quickly penetrate multiple layers of coatings. Methylene Chloride does not deplete the ozone layer and is considered to make negligible contributions to smog formation, the green-house effect and acid rain. Like other organic solvents, methylene chloride can be harmful to human health if used improperly. This study compares the performance of methylene chloride to 22 alternative solvents currently used in non-methylene chloride paint removers or solvents that have been proposed as replacement by chemical manufacturers. The performance of 26 non-methylene chloride paint remover commercial products and 5 lab-prepared formulations were compared to methylene chloride based paint removers.

When assessing viability of a paint remover, it must be considered that older paint is the usual substrate to be removed which is more chemically resistant than many paints available today. While latex paints are widely available now and more easily removed, they were not common 30 or more years ago. However, chemically resistant coatings are still used today. This study focused on the more difficult, chemically resistant finishes.

A chemical paint remover is composed of a mixture of solvents. The solvents in the paint remover diffuse into the paint causing the paint to swell and loosen from the substrate. Diffusion and solvency properties are key factors in the ability of a solvent to remove paint. Diffusion is the spontaneous movement of the solvents from an area of high concentration to an area of low concentration. The spontaneous movement of the solvent occurs as a result of the random kinetic movement of the solvent and does not require the input of energy. In general, smaller and less polar molecules will have a higher diffusion rate when compared to larger, more polar molecules. The second key factor in determining

the performance of a paint remover is the solubility of the paint resin in the solvent. The solvent must have the ability to swell or dissolve the paint film in order to be an effective paint remover.
To establish the performance criteria of methylene chloride based paint removers, the label copies from several manufacturers were evaluated for consumer benefits. The three most important criteria include:

(a) Removal of many types of coatings including oil based and epoxy paints for architectural coatings and factory applied OEM automotive paints
(b) Removal of multiple layers of coatings
(c) Fast removal of the coating, starts working within 15 minutes

Other criteria considered in the evaluation of paint remover is the cost and the VOC content of the paint remover. CARB regulations limit the VOC content of paint removers to 50 percent by weight.

2. Materials and Methods

Solvent Selection – The solvents used in this study were selected among solvents currently used in non-methylene chloride paint removers, solvents recommended as methylene chloride replacements by chemical manufacturers, and the list of EPA exempt solvents. Technical grade samples of the solvents were obtained and used in this study without further purification.

Paint Remover Selection – The paint removers used in this study were purchased from hardware stores or from suppliers on the internet. All paint removers were used as is.

Experimental Paint Removers – Through previous work screening neat solvents, several solvents were selected as having some paint remover potential. These solvents were formulated into paint removers that meet the 50% VOC requirement. These Experimental Paint Removers are:

A - a solvent based remover based on toluene, methanol, and acetone (50% VOC)
B - a solvent based remover based on 1,2-trans-dichloroethylene and acetone (50% VOC)
C - a solvent based remover based on 1,3-dioxalane and acetone (50% VOC)
D – an emulsion remover based on benzyl alcohol in water
E – an emulsion remover based on dibasic acids in water.

Paint Selection - The paints used in this study were purchased from local hardware or paint stores and were selected to represent chemically resistant paints commonly encountered in paint removal applications in household and in industrial applications. The paints purchased for this study are listed in Table 1 along with numbers of layers of paint used on the test panel. Only one type of paint was used for each test panel.

Table 1. List of paint, paint type and number of coatings used in study

Paint	Paint Type	Number of Coatings
Rust-Oleum Professional High Performance Protective Enamel Exterior Gloss	Oil-based alkyd paint	5
Sherwin Williams Macropoxy 646	Two component oil-based epoxy paint	3

Panel Preparation Procedure - Sanded birch plywood (1/2 in x 4-ft x 4-ft) was cut to approximately 12 x 8 inch panels. A 4-inch multi-purpose paint roller was used to apply coats designated paint to the birch panels as determined in Table 1. Each layer of paint was allowed to dry for four hours at ambient conditions then placed overnight in a laboratory oven at 50°C. Each layer of paint was tinted a different color to increase visibility of layers as they are stripped away. The panels were then aged for 30 days at ambient conditions before testing. These panels represent relatively fresh paint, actual paint that has cured for decades would be considerably more chemical resistant. After preparation the panels were stored at ambient conditions until needed for the stripping test.

Automotive Panel Preparation - The front hood from a 2006 Chevrolet Impala SS was purchased in good condition with factory paint intact. The hood was cleaned with a damp cloth and used in testing without further modifications.

Neat Solvent Testing

Apparatus

A grid was marked on each panel with masking tape creating test cells approximately 1 ½ in x 1 ½ in for the stripping trials. Each cell was labeled with the name of the solvent tested and duration time of the test. A C31 Large Commercial Sponge from 3M was cut to approximately sized ¼ in x 1 ½ in x 1 ½ in pieces. The sponge pieces were placed on each test cell to control evaporation and retain solvent in the test area.

Sample Preparation

For each sample, 2mL of solvent was applied to the sponge. Additional solvent was placed on the sponges at intervals to ensure that the solvent remained on the surface. At the timed intervals the test area was scraped using a plastic scraper and evaluated for effects on the coating and the number of layers of paint removed was recorded.

Paint Remover Testing

Apparatus

A grid was marked on each panel with masking tape creating test cells approximately of 1 ½ in x 1 ½ in for the stripping trials. Each cell was labeled with the name of the paint remover tested and duration time of the test.

Sample preparation

For each sample, 2mL of paint remover was applied to the cell. At the timed intervals the test area was scraped using a plastic scraper and judged for effects on the coating and the number of layers of paint removed was recorded.

3. Results

Test results of 22 alternative solvents and methylene chloride to remove multiple layers of oil-based alkyd and solvent-borne epoxy paint are listed in Appendix 1. Only methylene chloride was able to remove all five layers of oil based alkyd paint in 15 minutes. Methylene chloride removed two layers of the solvent-borne epoxy paint after 15 minutes and was the best performing solvent in all paint categories. Of the alternative solvents tested, trans-1,2 dichloroethylene and 1,3 dioxolane performed the best, but were shown to be far less effective than methylene chloride.

For automotive coatings the performance of methylene chloride was compared to five alternative solvents and the results are presented in Appendix 2. The two alternative solvents which performed the best on the wood panel test, trans-1,2 dichloroethylene, and 1,3 dioxolane were selected along with n-methyl-2-pyrrolidone, benzyl alcohol and a dibasic ester mixture, which are used in commercially available non-methylene chloride paint removers. Methylene Chloride was the only solvent that stripped the clear and top coat of the automotive finish in 15 minutes. Trans-1, 2 dichloroethylene and 1,3 dioxolane stripped the clear and top coat of the automotive finish in 30 minutes. None of the neat solvents, including methylene chloride, were able to strip all layers of the automotive coating including the primer. Only a formulated product would remove all layers. The remaining alternative solvents, n-methyl-2-pyrrolidone, benzyl alcohol and the dibasic ester mixture, had no stripping effect on the automotive coating after four hours.

Test results for the 26 non-methylene chloride paint removers and three methylene chloride paint removers in the removal of multiple layers of oil-based alkyd and oil-based epoxy paint are presented in Appendix 3. On the oil-based alkyd paint, methylene chloride paint removers were very effective when considering stripping depth and time to strip. The methylene chloride paint removers removed all layers in five minutes. In contrast, in the span of one hour, only one of the non-methylene chloride paint removers removed all layers of the oil-based alkyd paint. Over 4 hours later, 12 of the alternative paint removers removed all layers. On the solvent-borne epoxy paint, two methylene chloride paint removers removed two of the layers of paint in 15 minutes. The non-methylene paint removers had no stripping effect on the epoxy paint after four hours.

Test results for the five industrial strength non-methylene chloride paint removers and three methylene chloride paint removers in the removal of an automotive coating are presented in Appendix 4. The methylene chloride paint remover specifically designed to strip automotive finishes removed the clear, base and primer coats in 15 minutes. None of the alternate paint removers stripped paint down to bare metal.

4. Conclusion

Results from this study show that none of the alternative solvents are adequate as a replacement for methylene chloride on chemically resistant coatings.

In considering the neat solvents Methylene Chloride was faster at attacking the alkyd coating and much faster at attacking the epoxy coating. On the Automotive panel, methylene chloride was also faster than all others but no neat chemical, including methylene chloride, was able to remove all layers. Of the chemicals showing some attack on the coating, all have significant health or safety issues including flammability, reproductive hazards, and skin absorption hazards. Additionally, all of these except acetone are significantly (3-5 times) more expensive than methylene chloride.

The results from the formulated removers were even more revealing. No removers performed nearly as well as methylene chloride in "Time to Remove" on the Alkyd Paint. On Epoxy and Automotive Paints, the results were even more differential; no non-methylene chloride removers were able to completely remove coatings.

Most of the alternate solvents/removers that show any effectiveness in stripping chemically resistant coatings have their own negative characteristics. Most are very flammable, which can be a significant hazard on applications such as paint removal where the removers are spread over an area and left to

work. These conditions greatly increase the likelihood of fire. Others (NMP) are reproductive hazards. DMSO is not only actively absorbed through the skin but promotes the absorption of other toxic ingredients included with the coating as well. Most contain VOC's which limit allowable active content to meet air quality standards contributing to poor product performance. In additions to poor product performance, the alternatives increase ozone emissions creating a significant threat to health and the environment. Methylene chloride is a VOC (volatile organic compound) exempt solvent since it has a low potential for the formation of ground level ozone.

The traditional acetone/toluene/methanol strippers used before methylene chloride's introduction were not tested at this time but historical experience has shown similar performance to tested alternatives.

Appendix 1: Results of solvent paint remover testing of the layers of alkyd and epoxy removed at the given time.

Chemical (Neat)	Alkyd (5)			Epoxy (3)		
	15 min	30 min	1 hrs	15 min	30 min	1 hrs
methylene chloride	5	5	5	2	2	2
trans-1,2 dichloroethylene	5	5	5			
1,3 dioxalane	5	5	5			2
n-methyl-2-pyrrolidone		5	5			
acetone	5	5	5			
dimethoxymethane (methylal)		5	5			
n-butyl propionate			5			
dimethyl sulfoxide (DMSO)			4			
dimethyl carbonate						
benzyl methyl ether						
TOC (2,5,7,10 tetraoxaundecane)						
3-methoxy-3-methyl-1-butyl acetate (MMB-AC)						
Steposol MET-10U						
PCBTF/Oxsol 100						
3-methoxy-3-methyl-1-butanol (MMB)						
Eastman Omnia (butyl-3-hydroxybutyrate)						
benzyl alcohol						
dibasic esters (LVP)						
dibutoxymethane (butylal)						
propylene carbonate						
Elevance Clean 1200						
soya methyl ester						
glyercol formal						

No effect on Coating	
Slight softening but no removal with plastic scraper	
Difficult removal with much effort (number of layers listed)	2
Complete removal	5

Appendix 2: Results of solvent paint remover testing on OEM automotive paint

Chemical (Neat)	Automotive Coating			
	15 min	30 min	1 hrs.	4 hrs.
methylene chloride	1	1	1	1
trans-1,2 dichloroethylene	0	1	1	1
1,3 dioxolane	0	1	1	1
n-methyl-2-pyrrolidone	0	0	0	0
benzyl alcohol	0	0	0	0
dibasic esters (LVP)	0	0	0	0
No effect	0			
Stripped clear coat and top coat	1			
Stripped clear coat, top coat and base coat	2			

Appendix 3: Results of paint remover testing of the layers of alkyd and epoxy removed at the given times.

Company	Paint Remover	Ingredients (MSDS)	Flammable	Alkyd (5 Layers)				Epoxy (3 Layers)		
				5 min	15 min	30 min	1 hrs	15 min	30 min	1 hrs
W. M. Barr	Klean-Strip Premium Stripper	methylene chloride/methanol/Stoddard solvent	N	5	5	5	5	2	2	2
	Experimental Paint Remover A	toluene/acetone/methanol	Extremely	0	5	5	5	0	0	0
	Experimental Paint Remover B	1,2 trans dichloroethylene/acetone/methanol	Extremely	0	5	5	5	0	0	0
	Experimental Paint Remover C	1,3 dioxolane/acetone/methanol	Extremely	0	5	5	5	0	0	0
	Citristrip Safer Paint & Varnish Stripping Gel	NMP/DBE	N	0	0	0	5	0	0	0
	Experimental Paint Remover D	benzyl alcohol emulsion	N	0	0	0	0	0	0	0
	Experimental Paint Remover E	DBE emulsion	N	0	0	0	0	0	0	0
Dumond	Peel Away 1	calcium hydroxide/magnesium hydroxide/sodium hydroxide	N	0	0	1	3	0	0	0
	Peel Away 5 Soy Based	benzyl alcohol/NMP/soya methyl ester/DBE	N	0	0	0	0	0	0	0
	Peel Away 7	benzyl alcohol/NMP/DBE?	N	0	0	0	0	0	0	0
	Smart Strip	water/benzyl alcohol	N	0	0	0	0	0	0	0
	Smart Strip Pro	water/benzyl alcohol/formic acid	N	0	0	0	0	0	0	0
Ecoprocote	EcoFast HD Heavy Duty Paint Stripper	water/benzyl alcohol	N	0	0	0	0	0	0	0
EZ Strip	EZ Strip Paint and Varnish Stripper	DBE/triethyl phosphate	N	0	0	0	0	0	0	0
Franmar	Soy-Gel Paint and Urethane Remover	NMP/DBE/soy ester	N	0	0	0	0	0	0	0
Motsenbocker	Lift Off Paint and Varnish Remover	acetone/trade secret ingredients	N	0	0	0	0	0	0	0
Packaging Service Co	Crown Paint Strip Next	DBE/DMSO	N	0	0	0	0	0	0	0
PPG	DuraPrep 200 Coating Remover (Gel)	benzyl alcohol/solvent naphtha/2-aminoethanol/nonylphenol, branched ethoxylated	N	0	0	0	0	0	0	0
	DuraPrep 240 Industrial Coating Remover (Gel)	benzyl alcohol/hydrogen peroxide/solvent naphtha/glycollic acid/malic acid/barium bis(dinonylnaphthalenesuphonate)/amines, coco alkyl, ethoxylated	N	0	0	0	0	0	0	0
	DuraPrep Prep 400 Overspray Remover	benzyl alcohol/petroleum distillates/glycolic acid/quaternary ammonium compounds/hydrogen proxide	N	0	0	0	0	0	0	0
Solvent Kleene	D-Zolve 1012 Powder Coating Remover (immersion tank)	alkyl methyl ester/potassium hydroxide/cyclic amide	N	0	1	2	2	0	0	0
	D-Zolve 15-33R (aircraft)	alkyl methyl ester/petroleum naphtha/benzyl alcohol/methyl phenyl ether	N	0	0	0	0	0	0	0
Sunnyside	Multi-Strip Professional Paint Remover	DBE/NMP/formic acid	N	0	0	0	0	0	0	0
	Ready Strip Pro	DBE/NMP/formic acid	N	0	0	0	0	0	0	0
	Ready Strip Safer Paint & Varnish Remover	DBE/NMP/formic acid	N	0	0	0	0	0	0	0
	Ready-Strip Spray	NMP/DBE/monoethanolamine	N	0	0	0	0	0	0	0
	Ultri-Strip	DBE/NMP/formic acid	N	0	0	0	0	0	0	0
This Stuff Works, Inc.	TSW2 Multi-Master	NMP/DBE	N	0	0	0	0	0	0	0
	TSW2G Multi-Master (Gel)	NMP/DBE	N	0	0	0	0	0	0	0
	TSW3G (GEL) Mason-Master	potassium hydroxide/butyl cellosolve	N	0	0	1	1	0	0	0
	TSW9 Plasti-Master	DBE/proprietary surfactant	N	0	0	0	0	0	0	0
Zinsser	Magic Strip Citrus-Action	NMP/DBE/d-limonene	N	0	0	0	0	0	0	0

No Removal	
Some Removal	
All layers Removed	

Appendix 4: Results of non-methylene chloride paint remover testing of the layers of OEM automotive finish at the given time

Company	Paint Remover	Ingredients (MSDS)	Automotive Coating		
			15 min	30 min	1 hrs
W.M. Barr	Klean-Strip Aircraft Remover	methylene chloride/methanol/Tall oil/ammonium hydroxide/xylene	2	2	2
	Experimental Toluene Based Paint Remover	toluene/acetone/methanol	0	1	1
	Experimental 1,2 Trans Dichloroethylen Based Paint Remov	1,2 trans dichloroethylene/acetone/methanol	0	1	1
	Experimental 1,3 Dioxolane Based Paint Remover	1,3 dioxolane/acetone/methanol	0	1	1
	Smart Strip	water/benzyl alcohol	0	0	0
	EZ Strip Paint and Varnish Stripper	DBE/triethyl phosphate	0	0	0
	Citristrip Safer Paint & Varnish Stripping Gel	NMP/DBE	0	0	0
PPG	DuraPrep 200 Coating Remover (Gel)	benzyl alcohol\solvent naphtha/2-aminoethanol/nonylphenol, branched ethoxylated	0	0	0
	DuraPrep 240 Industrial Coating Remover (Gel)	benzyl alcohol/hydrogen proxide/solvent naphtha/glycollic acid/malic acid/barium bis(dinonylnaphthalenesuphonate)/amines, coco alkyl, ethoxylated	0	0	0
	DuraPrep Prep 400 Overspray Remover	benzyl alcohol/petroleum distillates/glycolic acid/quaternary ammonium compounds/hydrogen proxide	0	0	0
Solvent Kleene	D-Zolve 1012 Powder Coating Remover (immersion tank)	alkyl methyl ester/potassium hydroxide/cyclic amide	0	0	0
	D-Zolve 15-33R (aircraft)	alkyl methyl ester/petroleum naphtha/benzyl alcohol/methyl phenyl ether	0	0	0

No effect	0
Stripped clear coat and top coat	1
Stripped clear coat, top coat and base coat	2